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Imaging of single polymer chains based on their elasticity

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In this work we apply a force modulation technique to a standard atomic force microscope (AFM) in order to study the elasticity of individual polystyrene molecules. The sample mounted on a piezoelectric tube was forced to vibrate along the z direction. The corresponding modulation of the cantilever, which reflects the spring constant of the sample, was phase sensitively detected and measured as a function of the surface topography. The image contrast in these images is based on local variations of the surface elasticity. Compared to the conventional AFM topography image, the elasticity image shows an enhanced contrast with pronounced molecular structure. © 1994 American Institute of Physics.

Atomic force microscopy (AFM),¹ has proven to be a powerful technique to image solid state surfaces. Due to the relatively high forces (10^{-7} – 10^{-6} N) applied during operation of the AFM, imaging of soft materials in the contact mode suffers from insufficient image contrast. In the noncontact mode, however, lower forces are exerted (about 10^{-10} N) and the AFM becomes suitable for imaging soft materials but unfortunately with clearly less spatial resolution. As demonstrated in this work, this difficulty can be overcome by applying a force modulation technique.^{2,3} In this way the viscoelastic properties of soft organic molecules are used and a good image contrast even with molecular resolution is possible. In this operating mode of the AFM, the tip probes the local elastic properties of the surface resulting in an elasticity image.

Here we present a study of mechanical and viscoelastic properties of polymers at the single chain level. The polymer system investigated is based on self-assembling monolayers (SAMs) of organic thiols on gold. This kind of monolayers has proven to be useful for surface modifications directed at influencing surface properties such as wetting, adhesion, lubrication, and colloidal stabilization. SAMs based on organic sulfur compounds have been extensively studied.^{4–10} Organic thiols chemisorbed onto gold surfaces form a densely packed, crystalline like structure in which the alkyl chains are slightly tilted with respect to the surface normal. The thiol group is believed to bond covalently to the gold surface through a gold-thiolate bond. So far, most of the work with SAMs has been devoted to synthesizing suitable alkane thiols, sulfides, and disulfides with different lengths, various tail groups and polymers.¹¹ The use of mixed SAMs allows an even more detailed control of the physical and chemical properties of solid state surfaces.^{7,8}

When a gold substrate is brought into contact with a solution containing a mixture of short alkanethiols and thiol-terminated polystyrene (PSSH, see Fig. 1), a mixed monolayer is formed in which the polymer chains are randomly distributed. By varying the relative concentrations of the two components in solution, the grafting density of the polymer can be changed. In this way it is possible to graft polymer chains to the gold substrate in a controlled and permanent manner. To our knowledge, this is the first system which

enables covalent grafting of polymers with good control over the grafting density, which makes it a unique system also for investigations with scanning probe techniques. Using atomic force microscopy, single polymer molecules can be imaged in the collapsed state and it is feasible to address a single polymer chain, terminally attached to the gold surface. Thus a suitable system for single chain experiments with scanning probe techniques is introduced and it is to be expected that properties of individual macromolecules can be determined.

For our investigations, thiol terminated polystyrene (PSSH) was synthesized by anionic polymerization.¹¹ The molecular weight, M_w , of the resulting PSSH was determined to be 48 800 g/mol. The adsorption solutions of the desired mole fractions were prepared by keeping the PSSH concentration at 2 mg/ml and adding the appropriate amount of dodecanethiol, using toluene as a solvent. Gold substrates were exposed to the solution for 24 h and washed with fresh toluene afterwards. They were then dried under a stream of argon and placed in vacuum at 50 °C for 1 h. The substrates were stored under nitrogen. Figure 2 shows a schematic drawing of the adsorbed mixture of short molecules and long polymer chains on the substrate. The flat Au(111) substrates were prepared by epitaxial growth of 35 nm of gold on freshly cleaved mica substrates at 400 °C. In order to obtain isolated single chains of PSSH molecules, the ratio χ of the number of moles of PSSH over the total number of moles of the two adsorbing components was varied from 0.80 to 1.00. Single isolated polystyrene molecules could be obtained at $\chi < 0.97$. More details concerning the preparation of the mixed monolayers and their imaging with AFM will be published elsewhere.¹²

The atomic force/elasticity measurement have been per-

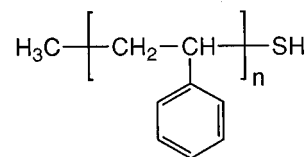


FIG. 1. The PSSH molecules used in this study.

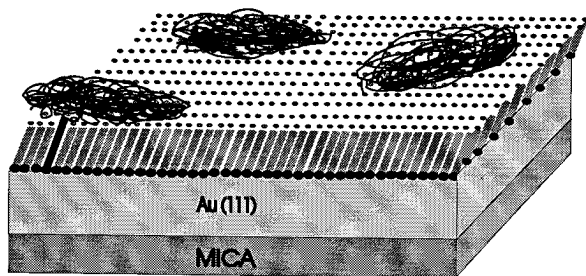


FIG. 2. Schematic drawing of the mixed self assembling monolayer (SAM) of PSSH molecules and dodecanethiol molecules on the underlying Au(111) surface.

formed under ambient conditions by using a commercially available AFM. In our experiment the sample was mounted on the top of the piezoelectric tube. A two segment photodiode was used to measure the deflection of the laser beam reflected from the back of the cantilever. A microfabricated Si_3N_4 cantilever with a spring constant of 0.1 N/m was used. The AFM used was slightly modified to measure the variations of the sample elasticity as well as the surface topography. In this operating mode the sample height was modulated by applying an ac voltage from a function generator to the piezoelectric z tube. The modulation amplitude (ΔZ_p) was chosen to be very low (about 1 Å). The frequency was chosen in the range of 10 kHz so as to be well above the cutoff frequency of the feedback loop and to give a good signal-to-noise ratio in the elasticity image. The height modulation was applied during scanning the stylus on the sample while the feedback loop was keeping the average force constant. The cantilever deflection ΔZ_c caused by the sample modulation (ΔZ_p) was measured phase sensitively by a lock-in amplifier. Consequently, the surface is deformed by the amount

$$\Delta Z_{\text{eff}} = \Delta Z_p - \Delta Z_c.$$

Measuring ΔZ_c and drawing it simultaneously with the topography will result in an image based on the contrast provided by the elasticity of the sample. ΔZ_c will be relatively small on soft and larger on hard surfaces. With a sample having a spring constant K_s and a cantilever of spring constant K_c the variation in the force acting on the surface is given by

$$\Delta F = K_s(\Delta Z_p - \Delta Z_c) = K_c \Delta Z_c.$$

Rearrangement of the above expression will result in the spring constant of the sample

$$K_s = K_c \left(\frac{\Delta Z_p}{\Delta Z_c} - 1 \right)^{-1}.$$

This value would directly give information about the elastic properties of the surface.

Neglecting adhesion forces, the surface modulus E of a sphere of radius R pressed by the amount ΔZ_{eff} is given by

$$E = \frac{K_c \Delta Z_c}{\sqrt{R(\Delta Z_{\text{eff}})^3}}.$$

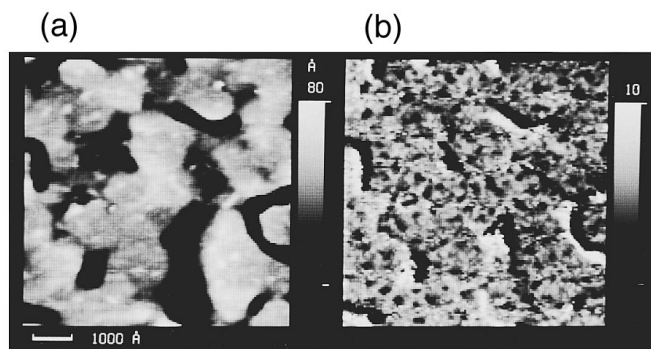


FIG. 3. (a) AFM topography image of single polymer chains in a mixed monolayer of thiol terminated polystyrene and dodecanethiol taken in the attractive regime of the contact mode. The black to white height difference corresponds to 80 Å reflecting mainly the height difference between the deep troughs (black areas) and the flat gold islands of the 350-Å-thick gold layer. (b) Simultaneously acquired elasticity image of the mixed monolayer presented in (a) by a force modulation technique. Single polymer chains can be recognized by the dark spots which indicate that the polymer molecules are softer than the dodecanethiol monolayer.

Since in AFM experiments adhesion forces are important, an exact determination of the surface modulus is not straightforward, however.

The force modulation mode is comparable to the spectroscopy mode of the STM where the sample height is modulated and the corresponding modulation of the tunneling current is measured (determination of the local work function Φ).

AFM images [Fig. 3(a)] obtained in the contact mode show with molecular resolution the single chains of PSSH molecules. The molecules are believed to correspond to the protrusions on the otherwise flat gold terraces coated with the dodecanethiol molecules. Figure 3(b) represents the elasticity image simultaneously taken. The dark spots in the position of the protrusions in Fig. 3(a) represent soft locations indicating that the PSSH molecules are softer than the layer of dodecanethiol molecules. The measured values of the apparent sample spring constant are in the range of 0.06 N/m for the soft (dark) locations and 0.1 N/m for hard (bright) locations. These represent hardly the actual values of the adsorbed films because of strong adhesion forces between tip and sample. A remarkable feature of the elasticity image is the good contrast. While increasing the force, no (or a very weak) contrast is obtained in the conventional AFM-topography image, a convenient contrast is found at the same location in the elasticity image [see Figs. 4(a) and 4(b)]. Elasticity images on the dodecanethiol-coated gold layers result in a homogeneous (flat) structure, indicating that the dodecanethiol molecules cover the entire gold surface.

The occasional ability to image the PSSH molecules using the AFM-topography mode indicates that a strong deformation of the molecules is occurring, which leads to the disappearance of the contrast. The molecules, apparently, retain their elastic properties, resulting in a clear contrast in the elasticity image. One of the possible contrast mechanisms which could explain this observation is a deformation of the PSSH molecules due to the high pressure exerted by the tip in the repulsive regime (about 10^{10} N/m²). The compressed

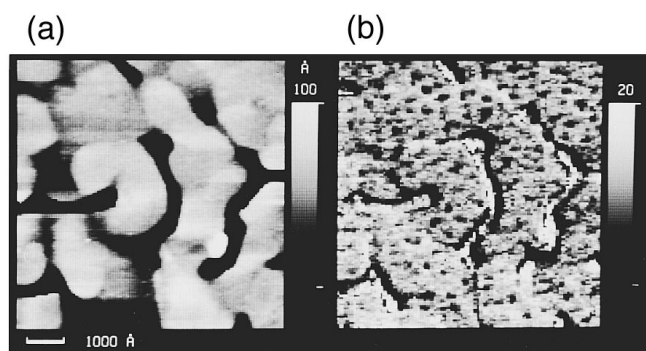


FIG. 4. In the repulsive regime of the attractive mode no contrast at all is observed in the conventional AFM-topography image (a) but a convenient contrast at the same location in the elasticity image is prominent (b).

part of the molecule will be forced to deviate to a lower pressure zone. Its height directly under the tip is now drastically reduced and a weak or even no contrast in the AFM image results [Fig. 4(a)]. However, the spring constant of the strongly deformed polymer molecule still differs from its surroundings. Since the applied force modulation technique is sensitive to the variations in spring constant of the sample, a convenient contrast in the elasticity image is produced. On the other hand, lowering the force exerted by the tip leads apparently to less deformation and consequently to an increase in the apparent height [see the protrusions in Fig. 3(a)]. A comprehensive study concerning the deformation of soft objects by the AFM tip is given by Weisenhorn *et al.*¹³

The AFM/elasticity measurements indicate that the mole fraction of the PSSH molecules on the gold surface is approximately 1.10^{-4} . This estimation is based on a surface area of 22 Å of the adsorbed dodecanethiols.¹⁴ This estimated mole fraction is orders of magnitude smaller than the mole fraction in the solution (0.97). This might be understood by taking into account that (I) the dodecanethiol mol-

ecules diffuse faster than the much larger PSSH macromolecules, (II) the long polystyrene chain shields its polar thiol group.

In summary, we have imaged for the first time single polystyrene molecules by their elastic properties. For imaging soft organic molecules the force modulation technique of the AFM turned out to be more sensitive than the conventional topography mode. Investigating single polymer chains may open the way for direct determination of single chain elastic properties under various conditions; a fascinating prospect.

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